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(54) A process for the preparation of oxygen-containing organic compounds and paraffinic hydrocarbons

(57) Syngas with a H₂/CO mol. ratio of at least 0.5 is partly converted in a first stage into oxygenates and the unconverted syngas having as such or after adjustment a H₂/CO molar ratio of at least 1.5 is converted in a second stage into paraffins over a Ni-, Co-, or Ru-Fischer-Tropsch catalyst.

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SPECIFICATION

A process for the preparation of oxygen-containing organic compounds and paraffinic hydrocarbons

The invention relates to a process for the preparation of oxygen-containing organic compounds and paraffinic hydrocarbons from a mixture of carbon monoxide and hydrogen. 5

Oxygen-containing organic compounds such as methanol, ethanol and dimethyl ether are valuable end products, and intermediate products, for instance for the preparation of aromatic hydrocarbons and lower olefins. The said oxygen-containing organic compounds can be prepared by catalytic conversion of mixtures of carbon monoxide and hydrogen with an H_2/CO molar ratio of at least 0.5. A drawback of these reactions is that they are thermodynamically strongly limited, so that a considerable part of the H_2/CO mixture is not converted. According as higher space velocities are used in the processes, lower conversions are obtained. It is true that a higher conversion can be reached by recycling the unconverted H_2/CO mixture, but recycling on a technical scale is an expensive process, which should be avoided if at all possible. Moreover, recycling the unconverted H_2/CO mixture entails another serious drawback. As a rule, the reaction product contains in addition to oxygen-containing organic compounds formed and unconverted hydrogen and carbon monoxide a considerable amount of carbon dioxide. This carbon dioxide has formed by the reaction of water with carbon monoxide according to the known CO-shift reaction. The water required for the CO-shift reaction may originate from an external source or may have been formed in the preparation of the oxygen-containing organic compounds. Addition of water to the H_2/CO mixture in order to make the CO-shift reaction proceed is carried out if the available H_2/CO mixture has too low an H_2/CO molar ratio. According to the CO-shift reaction the CO content falls and the H_2 content rises, resulting in an increase of the H_2/CO molar ratio. The CO-shift reaction can be carried out as an external shift (also designated pre-shift), in which the H_2/CO mixture to be converted, together with added water, is first conducted over a separate CO-shift catalyst, before being contacted with the catalyst which has activity for the conversion of an H_2/CO mixture into oxygen-containing organic compounds. As the latter catalysts generally have CO-shift activity as well, an external shift can be omitted in a number of cases and the desired increase of the H_2/CO molar ratio of the feed can be achieved simply by conducting this feed together with added water over the catalyst which has activity for the conversion of an H_2/CO mixture into oxygen-containing organic compounds. It is also the CO-shift activity of the latter catalyst which is responsible for the formation of carbon dioxide, if water is formed in the preparation of the oxygen-containing organic compounds. This situation presents itself if ether is formed in the preparation of oxygen-containing organic compounds. To avoid the building up of carbon dioxide in the process, the carbon dioxide should be removed from the recycle stream. Removal of carbon dioxide from recycle streams on a technical scale is, just as the recycling itself, an expensive process. 35

The applicant has carried out an investigation to find out to what extent it is possible in the preparation of oxygen-containing organic compounds to realize by catalytic conversion of an H_2/CO mixture a high conversion of the H_2/CO mixture into valuable organic compounds, without the necessity of recycling the unconverted H_2/CO mixture and removing the carbon dioxide. This possibility was indeed found to exist. To this end carbon monoxide and hydrogen present in the reaction product obtained in the catalytic conversion of the H_2/CO mixture into oxygen-containing organic compounds, if desired together with other components of this reaction product, should be contacted with a monofunctional catalyst containing one or more metal components with catalytic activity for the conversion of an H_2/CO mixture into paraffinic hydrocarbons, which metal components have been chosen from the group formed by cobalt, nickel and ruthenium. If the H_2/CO mixture that is available as the feed for the preparation of the paraffinic hydrocarbons has an H_2/CO molar ratio lower than 1.5, water should be added to this feed in an amount sufficient to bring the reaction with CO the H_2/CO molar ratio at a value of at least 1.5, and use should be made of a bifunctional catalyst combination which, in addition to containing the metal components with catalytic activity for the conversion of an H_2/CO mixture into paraffinic hydrocarbons, also contains one or more metal components with CO-shift activity. If the conversion of the H_2/CO mixture is carried out in this way, it is possible, using a high space velocity, to reach a very high conversion of the H_2/CO mixture into oxygen-containing organic compounds and paraffinic hydrocarbons. The paraffinic hydrocarbons obtained in the process are valuable as end product and as starting material for carrying out catalytic hydrocarbon conversion processes such as aromatization, isomerization, cracking and hydro-cracking. 55

The present patent application therefore relates to a process for the preparation of oxygen-containing organic compounds and paraffinic hydrocarbons, in which process a mixture of carbon monoxide and hydrogen with an H_2/CO molar ratio of at least 0.5 is contacted in a first step with a catalyst containing one or more metal components with catalytic activity for the conversion of an H_2/CO mixture into oxygen-containing organic compounds and in which process carbon monoxide and hydrogen present in the reaction product from the first step, if desired together with other components of this reaction product, are contacted in a second step with a monofunctional catalyst as defined above, on the understanding that if the feed for the second step has an H_2/CO molar ratio lower than 1.5, water is added to this feed in an amount sufficient to bring, by reaction with CO, the H_2/CO molar 60

ratio at a value of at least 1.5, and that in the second step use is made of a bifunctional catalyst combination as defined above.

The process according to the invention is highly flexible as regards the ratio of the amounts of oxygen-containing organic compounds to paraffinic hydrocarbons which can be prepared. If it is intended to effect the highest possible yield of oxygen-containing organic compounds, the circumstances under which the first step of the process is carried out can be chosen such that this wish is satisfied, and the unconverted H_2/CO mixture can be converted in the second step into paraffinic hydrocarbons. If it is intended to effect a high yield of paraffinic hydrocarbons, the circumstances under which the first step of the process is carried out can be chosen such that the reaction product of the first step contains a sufficient amount of unconverted H_2/CO mixture to guarantee in the second step the desired high yield of paraffinic hydrocarbons.

In the process according to the invention use is made of an H_2/CO mixture with an H_2/CO molar ratio of at least 0.5 as the feed for the first step. Such H_2/CO mixtures can very suitably be prepared by steam gasification of a carbon-containing material such as coal. The steam gasification is preferably carried out at a temperature of 900—1500°C and a pressure of 10—100 bar. Preferred H_2/CO mixtures are those with an H_2/CO molar ratio of 0.75—2.5. If the H_2/CO mixture there is available as the feed for the first step has an H_2/CO molar ratio lower than 0.5, water should be added to the H_2/CO mixture in an amount sufficient to bring, by reaction with CO, the H_2/CO molar ratio at a value of at least 0.5, and the mixture should be contacted with a catalyst having CO-shift activity. Adding water to the H_2/CO mixture and contacting the mixture with a catalyst having CO-shift activity is also possible in those cases where the H_2/CO mixture already has an H_2/CO molar ratio of at least 0.5, but where it is desirable to use an H_2/CO mixture with a higher H_2/CO molar ratio. The increase of the H_2/CO molar ratio can be carried out as a so-called external CO-shift, in which the water-containing H_2/CO mixture is contacted, in a separate step previous to the first step of the process according to the invention, with a separate catalyst with CO-shift activity. As the catalysts used in the first step of the process according to the invention as a rule have, in addition to their activity for the conversion of an H_2/CO mixture into oxygen-containing organic compounds, CO-shift activity, the increase of the H_2/CO molar ratio may also be carried out as an internal CO-shift, in which process the water-containing H_2/CO mixture is contacted directly with the catalyst in the first step of the process according to the invention. If in the process use is made of an external CO-shift, it is preferred not to apply carbon dioxide removal to the reaction product. In the first step of the process according to the invention an H_2/CO mixture which may contain water and/or carbon dioxide, is contacted with a catalyst containing one or more metal components with catalytic activity for the conversion of an H_2/CO mixture into oxygen-containing organic compounds. It is preferred to use in the first step a catalyst capable of converting an H_2/CO mixture into substantially methanol or dimethyl ether. Examples of suitable catalysts capable of converting an H_2/CO mixture into substantially methanol are catalysts containing:

- (a) zinc oxide and chromium oxide,
- (b) copper, zinc oxide and chromium oxide,
- (c) copper, zinc oxide and aluminium oxide, and
- (d) copper, zinc oxide, and oxides of rare earths.

Examples of suitable catalysts having the capability of converting an H_2/CO mixture into substantially dimethyl ether are catalysts containing one of the methanol synthesis functions under (a)—(d) and, in addition, an acid function, such as a physical mixture of gamma alumina and a composition containing copper, zinc oxide and chromium oxide. The first step of the process according to the invention is preferably carried out at a temperature of 175—350°C and a pressure of 30—300 bar and in particular at a temperature of 225—325°C and a pressure of 50—150 bar.

In the process according to the invention carbon monoxide and hydrogen present in the reaction product from the first step, if desired together with other components of this reaction product, are used as the feed for the second step. If necessary, the complete reaction product from the first step may be used as the feed for the second step. In the second step of the process according to the invention as much as possible of the CO present in the feed for the second step is to be converted into paraffinic hydrocarbons over a monofunctional catalyst containing one or more metal components with catalytic activity for the conversion of an H_2/CO mixture into paraffinic hydrocarbons, which metal components have been chosen from the group formed by cobalt, nickel and ruthenium. To this end the H_2/CO molar ratio in the feed for the second step should be at least 1.5 and preferably 1.75—2.25. If use is made of an H_2/CO mixture with a higher H_2/CO molar ratio as the feed for the first step, the first step of the process according to the invention can yield a reaction product in which an H_2/CO mixture is present which has an H_2/CO molar ratio of at least 1.5 and which is as such suitable for conversion over the said catalyst in the second step. An attractive way of ensuring that in the process according to the invention the reaction product from the first step has an H_2/CO molar ratio of at least 1.5, is adding water to the feed for the first step. Thanks to the CO-shift activity of the catalyst in the first step this water reacts with CO from the feed to form an H_2/CO_2 mixture. Adding water to the feed for the first step may be employed in the process according to the invention both in cases in which, without water addition, a reaction product would have been obtained from the first step with an H_2/CO molar ratio lower than 1.5, and in cases in which, also without water addition, a reaction product would have been obtained already

from the first step with an H_2/CO molar ratio of at least 1.5, but where it is desirable that the feed contacted with the catalyst in the second step should have a higher H_2/CO molar ratio.

If in the process according to the invention, whether or not after water addition to the feed for the first step, a reaction product is obtained from the first step with an H_2/CO molar ratio lower than 1.5, 5 water should be added to the feed for the second step in an amount sufficient to bring, by reaction with CO , the H_2/CO molar ratio at a value of at least 1.5, and in the second step use should be made of a bifunctional catalyst combination which, in addition to the metal components with catalytic activity for the conversion of an H_2/CO mixture into paraffinic hydrocarbons, also contains one or more metal components with CO -shift activity. The bifunctional catalyst combinations that may be used in the 10 second step of the process according to the invention are preferably composed of two separate catalysts, which for convenience will be designated catalyst A and catalyst B. Catalyst A is the one containing the metal components with catalytic activity for the conversion of an H_2/CO mixture into paraffinic hydrocarbons and which metal components have been chosen from the group formed by cobalt, nickel and ruthenium. Catalyst B is the one containing the metal components with CO -shift 15 activity. Both if a monofunctional catalyst is used and if a bifunctional catalyst combination is used in the second step of the process according to the invention, it is preferred to use as catalyst A a cobalt catalyst such as cobalt catalyst prepared by impregnation. Very suitable for the present purpose are catalysts that contain 10—40 pbw cobalt and 0.25—5 pbw zirconium, titanium or chromium per 100 pbw silica and which have been prepared by impregnating a silica carrier with one or more aqueous 20 solutions of salts of cobalt and zirconium, titanium or chromium, followed by drying the composition, calcining at 350—700°C and reducing at 200—350°C. Suitable B-catalysts are the usual CO -shift catalysts. In the bifunctional catalyst combinations the catalysts A and B may be present as physical mixture. When the second step of the process is carried out using a fixed catalyst bed, this bed is preferably built up of two or more alternating layers of particles of, successively, catalyst B and catalyst 25 A. Water addition to the feed for the second step together with the use of a bifunctional catalyst combination in the second step can be used in the process according to the invention both in cases in which the reaction product from the first step has an H_2/CO molar ratio lower than 1.5, and in cases in which the reaction product from the first step already has an H_2/CO molar ratio of at least 1.5, but where it is desired that the feed contacted in the second step with catalyst A should have a higher H_2/CO molar 30 ratio. The second step of the process according to the invention is preferably carried out at a temperature of 125—300°C and a pressure of 1—150 bar and in particular at a temperature of 175—275°C and a pressure of 5—100 bar. 17-30

The oxygen-containing organic compounds prepared in the two-step process can very suitably be used as starting material for the catalytic conversion into lower olefins and/or aromatic hydrocarbons. 35 This conversion is preferably carried out by contacting the oxygen-containing organic compounds at a temperature of 300—600°C, a pressure of 1—50 bar and a space velocity of 0.2—15 $kg \cdot kg^{-1} \cdot h^{-1}$ with a crystalline metal silicate as the catalyst. It is preferred to use in this conversion pressures of 1—10 bar.

Very suitable catalysts for the conversion of the oxygen-containing organic compounds are 40 crystalline metal silicates characterized in that after one hour's calcining in air at 500°C they have the following properties:

- (a) thermally stable up to a temperature of at least 600°C
- (b) an X-ray powder diffraction pattern showing as the strongest lines the four lines given in 45 Table A.

TABLE A

D(Å)	Relative intensity
11.1 ± 0.2	VS
10.0 ± 0.2	VS
3.84 ± 0.07	S
3.72 ± 0.06	S

wherein the letters used have the following meanings: VS = very strong; S = strong, and

- (c) in the formula which represents the composition of the silicate expressed in moles of the oxides, and in which in addition to oxides of hydrogen, alkali metal and silicon, one or more oxides of a 50 trivalent metal A chosen from the group formed by aluminium, iron, gallium, rhodium chromium and scandium are present, the SiO_2/A_2O_3 molar ratio (further designated M in this patent application) is more than 10. These crystalline metal silicates will in this patent application further be designated:

"silicates of type 1". The expression "thermally stable up to a temperature of at least $t^{\circ}\text{C}$ ", as used in this patent application, means that when the silicate is heated up to a temperature of $t^{\circ}\text{C}$, the X-ray powder diffraction pattern of the silicate does not substantially change. The silicates of type 1 can be prepared starting from an aqueous mixture containing the following compounds: one or more compounds of an alkali metal (M), one or more compounds containing a quaternary organic cation (R), one or more silicon compounds and one or more compounds in which a trivalent metal A chosen from the group formed by aluminium, iron, gallium, rhodium, chromium and scandium is present. The preparation of the silicates of type 1 is effected by maintaining the mixture at elevated temperature until the silicate has formed, separating it from the mother liquor and calcining it. In the aqueous mixture from which the silicates of type 1 are prepared the various compounds should be present in the following ratios, expressed in moles of the oxides:

$$\text{M}_2\text{O}:\text{SiO}_2 = 0.01-0.35,$$

$$\text{R}_2\text{O}:\text{SiO}_2 = 0.01-0.4,$$

$$\text{SiO}_2:\text{A}_2\text{O}_3 > 10, \text{ and}$$

$$\text{H}_2\text{O}:\text{SiO}_2 = 5-65.$$

Variation of the quaternary organic cation incorporated into the aqueous mixture yields silicates of type 1 which differs at significant points as regards their complete X-ray powder diffraction pattern.

The complete X-ray powder diffraction pattern of an iron silicate and of an aluminium silicate both prepared using a tetrapropylammonium compound is given in Table B.

TABLE B

d(Å)	Relative intensity	d(Å)	Relative intensity
11.1	100	3.84 (D)	57
10.0 (D)	70	3.70 (D)	31
8.93	1	3.63	16
7.99	1	3.47	<1
7.42	2	3.43	5
6.68	7	3.34	2
6.35	11	3.30	5
5.97	17	3.25	1
5.70	7	3.05	8
5.56	10	2.98	11
5.35	2	2.96	3
4.98 (D)	6	2.86	2
4.60	4	2.73	2
4.35	5	2.60	2
4.25	7	2.48	3
4.07	2	2.40	2
4.00	4		

(D) = doublet

The complete X-ray powder diffraction pattern of an iron silicate and of an aluminium silicate prepared using a tetrabutylammonium compound or a tetrabutylphosphonium compound is given in Table C.

TABLE C

d(Å)	Relative intensity	d(Å)	Relative intensity
11.1	100	3.84	65
10.0	70	3.70	20
7.42	2	3.63	<2
6.68	5	3.47	2
6.35	2	3.34	1
5.97	16	3.30	4
5.70	<1	3.05	5
5.56	8	2.98	9
4.98	6	2.86	1
4.60	3	2.60	2
4.35	5	2.48	3
4.25	<1	2.40	2
4.00	<1		

5 When silicates of type 1 are used as catalysts for the conversion of the oxygen-containing organic compounds, preference is given to silicates containing only one of the above mentioned trivalent metals and in particular to silicates containing as trivalent metal aluminium, iron or gallium. 5

Other very suitable catalysts for the conversion of the oxygen-containing organic compounds are the following crystalline aluminosilicates: faujasite, zeolite Y, zeolite X, mordenite, erionite, offretite, 10 zeolite ω , ferririte, chabazite and zeolite ZSM-34. These crystalline aluminosilicates will in this patent application further designated: "silicates of type 2". 10

Other very suitable catalysts for the conversion of the oxygen-containing organic compounds are silicates of type 1 or type 2 upon which one or more catalytically active metals have been deposited by impregnation or ion exchange. These crystalline silicates will in this patent application further be 15 designated: "silicates of type 3". Preference is given to silicates of type 3 upon which magnesium or manganese has been deposited. 15

If it is intended to convert the oxygen-containing organic compounds into substantially aromatic hydrocarbons, the conversion is preferably carried out at a temperature of 300—400°C and a space velocity of 0.5—5 kg · kg⁻¹ · h⁻¹ and the preferred catalyst is a silicate of type 1, whose m is less than 200. 20

If it is intended to convert the oxygen-containing organic compounds into substantially lower olefins, the conversion is preferably carried out either at a temperature of 400—600°C, a space velocity of 1—10 kg · kg⁻¹ · h⁻¹ and using as the catalyst a silicate of type 1, whose m is more than 200, or at a temperature of 300—500°C, a pressure of 1—5 bar, a space velocity of 0.2—2 kg · kg⁻¹ · h⁻¹ and 25 using as the catalyst a silicate of type 2 or type 3. 25

For the catalytic conversion of oxygen-containing organic compounds into lower olefins and/or aromatic hydrocarbons it is preferred to start from a feed of dimethyl ether or a mixture of oxygen-containing organic compounds consisting substantially of dimethyl ether. In addition to C₄⁻ olefins and C₅⁺ hydrocarbons, C₄⁻ paraffins are formed in the catalytic conversion of oxygen-containing organic 30 compounds. In the conversion it is desirable to suppress the formation of C₄⁻ paraffins as much as possible. An investigation by the Applicant has shown that in the catalytic conversion of the oxygen-containing organic compounds the selectivity to C₄⁻ paraffins is lower if the oxygen-containing organic compounds are not used as such as the feed, but diluted. Suitable diluents are, inter alia, water, carbon 30

monoxide, carbon dioxide, hydrogen and C_4^- paraffins.

The combination of the two-step process according to the invention with a process for the catalytic conversion of oxygen-containing organic compounds into lower olefins and/or aromatic hydrocarbons is very attractive, because the reaction product from the first step of the process

5 according to the invention contains at least a number of the above-mentioned diluents, viz.: unconverted hydrogen and carbon monoxide and further water and/or dioxide and/or C_4^- paraffins.

The combination of the two-step process according to the invention with a process for the catalytic conversion of oxygen-containing organic compounds into lower olefins and/or aromatic hydrocarbons may be carried in three ways.

10 According to the first embodiment the reaction product from the first step consisting of oxygen-containing organic compounds, hydrogen, carbon monoxide and a by-product containing carbon dioxide and/or water and/or C_4^- paraffins is separated into at least two fractions of which one contains all the oxygen-containing organic compounds and at least 50%v of the by-product, and one contains all of the hydrogen and carbon monoxide. The latter fraction may contain the rest of the by-product. The fraction

15 containing the oxygen-containing organic compounds is catalytically converted into lower olefins and/or aromatic hydrocarbons and the fraction containing hydrogen and carbon monoxide is catalytically converted in the previously mentioned second step of the process according to the invention. In this embodiment the reaction product from the first step is separated preferably into two fractions, of which one contains all the oxygen-containing organic compounds and all of the by-product, and the other

20 contains all of the hydrogen and carbon monoxide.

According to the second embodiment, at least all of the hydrogen, carbon monoxide and oxygen-containing organic compounds of the reaction product from the first step are together used as the feed for the second step of the process according to the invention. By preference, the complete reaction product from the first step is used as the feed for the second step. The reaction product of the second

25 step, which consists substantially of oxygen-containing organic compounds formed in the first step and of paraffinic hydrocarbons formed in the second step, and which contains in addition, inter alia, unconverted hydrogen and carbon monoxide, water and possible carbon dioxide, may be used as such as the feed for the additional process step in which catalytic conversion of the oxygen-containing organic compounds into lower olefins and/or aromatic hydrocarbons takes place. In view of the

30 possibility that part of the C_5^+ paraffinic hydrocarbons formed in the second step is converted in the additional process step into aromatic hydrocarbons, which may be undesirable, it is preferred to separate the C_5^+ hydrocarbons from the reaction product of the second step before using this reaction product as the feed for the additional process step.

According to the third embodiment, at least all of the hydrogen, carbon monoxide and oxygen-containing organic compounds of the reaction product from the first step are together contacted in the

35 additional process step with the catalyst converting the oxygen-containing organic compounds into lower olefins and/or aromatic hydrocarbons. By preference, the complete reaction product from the first step is used as the feed for the additional process step. Of the reaction product from the additional process step, which contains hydrogen, carbon monoxide, C_4^- olefins, a C_5^+ fraction rich in aromatics,

40 C_4^- paraffins, water and possibly carbon dioxide originating from the first step, at least hydrogen and carbon monoxide should be used as the feed for the second step of the process according to the invention. If desired, the complete reaction product from the additional process step may be used as the feed for the second step of the process according to the invention. It is preferred to separate the C_4^- olefins from the reaction product of the additional process step before using this reaction product as the

45 feed for the second step of the process according to the invention.

The Applicant has found that if in the second step of the process use is made of the previously mentioned cobalt-impregnation catalyst promoted with zirconium, titanium or chromium, a mixture of heavy paraffinic hydrocarbons is obtained, which is pre-eminently suitable for high-yield conversion into middle distillate by hydrocracking. The hydrocracking operation is characterized by a very low gas

50 production and hydrogen consumption.

The invention will now be explained with reference to the following example.

EXAMPLE

In the investigation use was made of the following catalysts.

55 Catalyst 1
A Cu/ZnO/Cr₂O₃ catalyst with a Cu/Zn/Cr atomic ratio of 5:3:2.

Catalyst 2
p-Al₂O₃ calcined at 800°C.

Catalyst 3
A Cu/ZnO/Al₂O₃ catalyst with a Cu/Zn atomic ratio of 0.55.

Catalyst 4

A Co/Zr/SiO₂ catalyst that contained 25 pbw cobalt and 0.9 pbw zirconium per 100 pbw silica and which had been prepared by impregnating a silica carrier with an aqueous solution containing a cobalt and a zirconium salt, followed by drying the composition, calcining it at 500°C and reducing it at 5 250°C. 5

Catalyst 5

A crystalline aluminium silicate which, after one hour's calcining in air at 500°C, had the following properties:

- (a) thermally stable up to a temperature of at least 800°C,
- 10 (b) an X-ray powder diffraction pattern substantially as shown in Table B, and 10
- (c) in the formula representing the composition of the silicate, expressed in moles of the oxides, the SiO₂/Al₂O₃ molar ratio was higher than 10.

CATALYST MIXTURE I

A physical mixture of catalyst 1 and catalyst 2 in a weight ratio of 1:1.

15 CATALYST MIXTURE II 15

A layer of catalyst 3 and a layer of catalyst 4 in a volume ratio of 1:2.

The catalysts 1 and 4 and the catalyst mixtures I and II were tested for the preparation of methanol or dimethyl ether in one step and for the preparation of paraffinic hydrocarbons and methanol or dimethyl ether in two steps. The test was carried out in one or two 50-ml reactors containing a fixed 20 catalyst bed. Seven experiments were carried out. The experiments 1, 2 and 4 were carried out in one 20 step; the other experiments were carried out in two steps. In all the experiments a pressure of 60 bar was used in the first step. In all the experiments carried out in two steps the complete reaction product from the first step was used as the feed for the second step. The feed for the first step of experiment 7 has been obtained from an H₂/CO starting mixture with an H₂/CO molar ratio of 0.5.

25 To this H₂/CO mixture so much water was added that after performing an external CO-shift over catalyst 3 an H₂/CO molar ratio of 1.0 was reached. The CO₂ formed in the CO-shift (14.3%v based on the gas mixture) was not separated off. The CO₂-containing H₂/CO mixture with an H₂/CO molar ratio of 1.0 was used as the feed for the first step of experiment 7.

The results of the experiments 1—7 are listed in Table D.

30 In experiment 8 a three-step process was simulated for the conversion of an H₂/CO mixture into aromatic hydrocarbons, lower olefins and paraffinic hydrocarbons, using the composition of the product from the first step of experiment 7 listed in Table D. 30

EXPERIMENT 8

35 The product from the first step of experiment 7 can be separated into two fractions, viz. a fraction A consisting of hydrogen and carbon monoxide with an H₂/CO molar ratio of 0.88 and a fraction B consisting of dimethyl ether, carbon dioxide and water in a volume ratio of 24.1:70.5:5.4. In experiment 8 the two fractions were converted separately. 35

Fraction A was conducted over catalyst mixture II at a temperature of 240°C, a pressure of 36 bar, a space velocity of 1000 Nl.1⁻¹ · h⁻¹ and with addition of 0.171 water per 1 catalyst per hour. The 40 conversion of the H₂/CO mixture was 87%v. When the conversion of the H₂/CO mixture in the first step of experiment 7 is taken into account, this means a total conversion of the H₂/CO mixture of 93%v. 40

Fraction B was conducted over catalyst 5 at a temperature of 500°C, and a pressure of 1 bar and a space velocity of 1 g dimethyl ether/g catalyst/h. The conversion of dimethyl ether was 100%. The hydrocarbon mixture formed had the following composition:

- 15 30%w of a C₅⁺ fraction rich in aromatics, 45
- 60%w of a C₄⁻ olefin fraction,
- 10%w of a C₄⁻ paraffin fraction.

Of the experiments 1—8 described above, only two-step experiments 3 and 5—7 and the three-step experiment 8 are experiments according to the invention. The one-step experiments 1, 2 and 4 are outside the scope of the invention. They have been included in the patent application for 50 comparison. 50

The following remarks can be made with regard to the results listed in Table D.

TABLE D

Experiment No.	1	2	3	4	5	6	7
Catalyst in the first step, No.	1	1	1	1	I	I	I
Amount of catalyst in the first step, ml	10	10	2.5	10	5	6	5
Temperature in the first step, °C	250	250	250	300	300	300	300
Space velocity of the H ₂ /CO mixture based on the total catalyst volume (1st + 2nd step), l.l ⁻¹ · h ⁻¹	4000	1000	1000	1000	1000	1000	1000
H ₂ /CO molar ratio in the feed for the first step	2.0	2.0	2.0	1.0	1.0	1.5	1.0
Amount of CO ₂ in the feed for the first step, %v	4	4	4	—	—	—	14.3
Conversion of the H ₂ /CO mixture in the first step, %v	41	56	41	66	48	40	46
<i>Composition of the product from the first step, %v</i>							
CO	27.0	23.4	27.0	30.4	38.2	27.3	33.4
H ₂	50.0	42.2	50.0	30.4	38.2	54.5	29.3
CH ₃ OH	17.6	28.1	17.6	—	—	—	—
CH ₃ OCH ₃	—	—	—	19.6	11.8	9.1	9.0
CO ₂	4.0	4.7	4.0	19.6	11.8	9.1	26.3
H ₂ O	1.4	1.6	1.4	—	—	—	2.0
H ₂ /CO molar ratio of the product from the first step	1.85	1.80	1.85 1.48	1.0 0.58	1.0 0.53	2.0 1.25	0.88 0.05
Catalyst in the second step, No.	—	—	4	—	II	4	II
Amount of catalyst in the second step, ml	—	—	7.5	—	5	4	5
Amount of water added to the feed for the second step, ml (1 cat. in the second step) ⁻¹ · h ⁻¹	—	—	—	—	140	—	170
Temperature in the second step, °C	—	—	230	—	240	240	240
Pressure in the second step, bar	—	—	40	—	45	40	55
Conversion of the H ₂ /CO mixture of the second step, %v	—	—	90	—	86	85	84

TABLE D—continued

Experiment No.	1	2	3	4	5	6	7
<i>Composition of the paraffinic hydrocarbon fraction of the product from the second step, %w</i>							
C ₄ ⁻	—	—	11.5	—	13	12.5	12
C ₅ —C ₁₂	—	—	30	—	33	33	32
C ₁₃ —C ₁₉	—	—	23	—	23	22.5	23
C ₂₀ ⁺	—	—	35.5	—	31	32	33
Total conversion of the H ₂ /CO mixture (1st + 2nd step), %v	41	56	94	66	93	91	91

The experiments 1 and 2 show the one-step preparation of methanol. In experiment 1 a low conversion of the H₂/CO mixture is reached (41%v). In comparison with experiment 1 the space velocity in experiment 2 has been reduced by a factor of 4. The result of experiment 2 shows that this causes an increase in the conversion of the H₂/CO mixture (from 41 to 56%v), but the conversion achieved is still much too low for using the process on a technical scale without recycling the unconverted H₂/CO mixture.

Experiment 3 demonstrates the preparation of methanol and paraffinic hydrocarbons using the two-step process according to the invention. With use of the same space velocity as in experiment 2 (now based on the total catalyst volume in the first step and the second step) a conversion of the H₂/CO mixture of 94%v is reached now.

Experiment 4 shows the one-step preparation of dimethyl ether. In comparison with experiment 2 (one-step preparation of methanol) the conversion of the H₂/CO mixture is higher now (66 instead of 56%v), but the conversion achieved is still far too low for using the process on a technical scale without recycling the unconverted H₂/CO mixture.

Experiments 5—7 show the preparation of dimethyl ether and paraffinic hydrocarbons using the two-step process according to the invention. In comparison with experiment 4, in experiment 5 a conversion of the H₂/CO mixture is reached of 93%v, using the same total amount of catalyst.

Experiments 5 and 6 demonstrate the two-step process according to the invention, starting from H₂/CO mixtures with different H₂/CO molar ratios. In view of the low H₂/CO molar ratio of the product from the first step of experiment 5 (1.0), water is added to the feed for the second step in this experiment.

Experiment 7 is a variant of experiment 5, in which the H₂/CO mixture with H₂/CO molar ratio 1.0, which is used as the feed for the first step, has been obtained by applying an external CO-shift to an H₂/CO mixture with an H₂/CO molar ratio of 0.5 and in which the CO₂ formed is not removed. Just as in experiment 5, in experiment 7 water is added to the feed for the second step in view of the low H₂/CO molar ratio of the product from the first step (0.88).

CLAIMS

1. A process for the preparation of oxygen-containing organic compounds and paraffinic hydrocarbons, characterized in that a mixture of carbon monoxide and hydrogen with an H₂/CO molar ratio of at least 0.5 is contacted in a first step with a catalyst containing one or more metal components with catalytic activity for the conversion of an H₂/CO mixture into oxygen-containing organic compounds and in that carbon monoxide and hydrogen present in the reaction product from the first step, if desired together with other components of this reaction product, are contacted in a second step with a monofunctional catalyst containing one or more metal components with catalytic activity for the conversion of an H₂/CO mixture into paraffinic hydrocarbons, which metal components have been chosen from the group formed by cobalt, nickel and ruthenium, on the understanding that if the feed for the second step has an H₂/CO molar ratio lower than 1.5, water is added to this feed in an amount sufficient to bring, by reaction with CO, the H₂/CO molar ratio at a value of at least 1.5 and that in the second step use is made of a bifunctional catalyst combination which, in addition to the metal components with catalytic activity for the conversion of an H₂/CO mixture into paraffinic hydrocarbons, also contains one or more metal components with CO-shift activity.

2. A process according to claim 1, characterized in that in the first step of the process use is made of a catalyst capable of converting an H₂/CO mixture into substantially methanol or dimethyl ether.

3. A process according to claim 1 or 2 characterized in that the first step of the process is carried out at a temperature of 225—325°C and a pressure of 50—150 bar.

4. A process according to any of claims 1—3, characterized in that the catalyst with activity for the conversion of an H_2/CO mixture into paraffinic hydrocarbons used in the second step of the process is a catalyst containing 10—40 pbw cobalt and 0.25—5 pbw zirconium, titanium or chromium per 100 pbw silica and has been prepared by impregnating a silica carrier with one or more aqueous solutions of salts of cobalt and zirconium, titanium or chromium followed by drying the composition, calcining at 350—700°C and reducing at 200—350°C. 5
5. A process according to any one of claims 1—4, characterized in that water is added to the feed for the second step and in that the second step is carried out using a fixed catalyst bed built up of two or more alternating layers of particles of successively the CO-shift catalyst and the catalyst having activity for the conversion of an H_2/CO mixture into paraffinic hydrocarbons. 10
6. A process according to any one of claims 1—5, characterized in that the second step is carried out at a temperature of 175—275°C and a pressure of 5—100 bar.
7. A process according to any one of claims 1—6, characterized in that the oxygen-containing organic compounds formed in the first step of the process are catalytically converted in an additional process step in the presence of a diluent into lower olefins and/or aromatic hydrocarbons. 15
8. A process according to claim 7, characterized in that the additional process step is carried out at a temperature of 300—600°C, a pressure of 1—50 bar, a space velocity of 0.2—15 $kg \cdot kg^{-1} \cdot h^{-1}$ and using a crystalline metal silicate as the catalyst.
9. A process according to claim 7 or 8, characterized in that for the preparation of substantially aromatic hydrocarbons from the oxygen-containing organic compounds the catalyst in the additional process step is a silicate of type 1, as defined hereinbefore, of which silicate m is less than 200. 20
10. A process according to claim 7 or 8, characterized in that for the preparation of substantially low olefins from the oxygen-containing organic compounds the catalyst in the additional process step is a silicate of type 1, as defined hereinbefore, of which silicate m is higher than 200, and in that the additional process step is carried out at a temperature of 400—600°C and a space velocity of 1—10 $kg \cdot kg^{-1} \cdot h^{-1}$. 25